Present and past calcium isotope fractionation in marine calcifying organisms

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Precise isotope analysis has developed to one of the most important tool in marine geochemistry. Accurate isotope fractionation is used for climate reconstructions for millions years back into the Earth's history.

Recent advances in thermal and plasma mass spectrometry have allowed the precise measurement of small differences in Ca isotope composition in $CaCO_3$. As a result, recent isotope studies of Ca biomineralization have been able to test whether Ca isotopes can provide an environmental indicator - e.g. of *T* - using marine $CaCO_3$ as an archive. It was hoped that development of this tool would provide information complementary to that gained from more traditional marine *T* data, such as Mg/Ca in foraminifera and Sr/Ca in corals. For both calcite and aragonite—two out of six polymorphs of $CaCO_3$—precipitation experiments have shown that $\Delta^{44/40}Ca_{CC\text{-}BS}$ (CC: Calcit; BS: Bulk Solution) for inorganic aragonite correlates with *T* (~0.02‰/ºC) (Fig. 1). However, aragonite displays an offset of ~-0.5‰ relative to calcite. In contrast, Ca isotope fractionation in biogenic $CaCO_3$ depends on more factors than simply polymorphism. Aragonitic sclerosponges and pteropods secrete skeletons with a fractionation factor similar to that for inorganic aragonite, whereas aragonitic scleractinian corals, calcitic coccolithophores, and calcitic planktonic foraminifera have comparable degrees of isotope fractionation, lying between the values for inorganic calcite and aragonite (Fig. 1). Two species of planktonic foraminifera, *G.s sacculifer* and *N.pachyderma* (sin.), show greater dependence of $\Delta^{44/40}Ca_{CC\text{-}GS}$ on T (Fig. 1). Given their different habitats (tropical versus polar surface ocean), both species show surprisingly similar T sensitivity (~0.24‰/ºC). This was observed in laboratory cultures and in planktic foraminifera collected from the ocean with tow samplers. However, other studies involving these same species failed to reproduce the large *T* dependence (Griffith et al., 2008a), suggesting an influence of salinity and *T* thresholds for the various species (Hippler et al., 2009). Latter observation indicates a complex and unpredictable physiological control on Ca uptake by calcifying organisms prior to $CaCO_3$ formation challenging its use as paleo-temperature proxy.

Calcium is provided to the ocean by rivers that drain mineral-weathering areas on the continents and by hydrothermal activity in the oceans. An additional source of Ca flux in the geological past was dolomitization (Heuser et al., 2005), in which Ca in $CaCO_3$ was replaced by Mg. In the modern ocean, the most important sinks for Ca are biogenic precipitation and sedimentary deposition of $CaCO_3$. Less important is the formation of $CaCO_3$ during low *T* alteration of ocean crust. The actual isotope compositions of Ca sinks and sources are similar, so the modern ocean is close to or at steady state (Schmitt et al., 2003). However, the situation must have been different in the geological past. For example, De La Rocha and DePaolo (2000) showed that

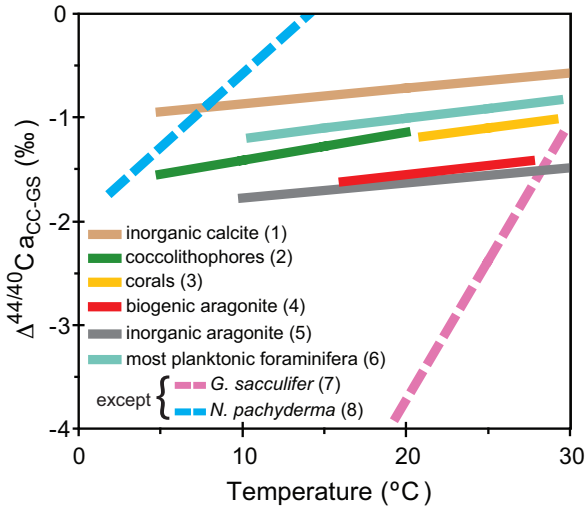

Figure 1:Temperature dependent Ca isotope fractionation in: 1) inorganic calcite 2) calcite of coccolithophores 3) aragonite skeletons of sceleractinian corals 4) aragonite shells of sclerosponges and pteropods 5) inorganic aragonite, 6) calcite of most planktonic foraminifera, 7) planktonic foraminifer Globigerinoides sacculifer, and 8) planktonic foraminifer Neogloboquadrina pachyderma (sin.).

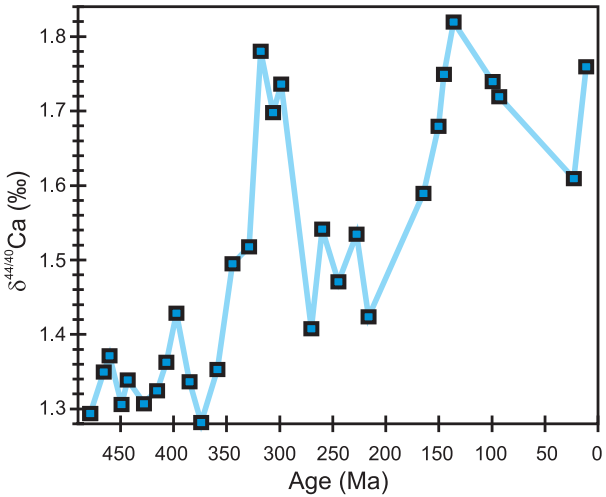

Figure 2: Phanerozoic history of seawater calcium isotope composition ($\delta^{44/40}Ca$) recorded in marine fossils (brachiopods and belemnites) and planktic foraminifera) are averaged in 10 million year bins. The record shows a general increase with time from low values in the Early Paleozoic (540 to 360 Ma) to high values in the Early Cretaceous (146 to 100 Ma) and Neogene (23 to 0 Ma). A sharp rise during the Carboniferous (360 to 300 Ma) and a second rise occurred during the Late Jurassic (160 to 145 Ma).

$\delta^{44/40}Ca$ varied considerably during the last 80 My. During the early Paleogene, relatively high $\delta^{44/40}Ca$ values reflected the fact that Ca input flux was ~80% of the output flux for a period of ~25 My, causing Ca concentration in seawater to decrease. Further studies confirmed that substantial fluctuations in the $\delta^{44/40}Ca$ of seawater occurred during the Neogene (c.f. Griffith et al., 2008b) and earlier in Earth history. Variations much longer than the Ca residence time (Fig. 2) cannot be explained by imbalances in the ocean Ca budget. In this regard, Heuser et al. (2005) suggested that the formation of dolomite [$MgCa(CO_3)_2$] leads to isotope fractionation as Ca is replaced by Mg in marine $CaCO_3$. The enrichment of dolomite in heavy Ca isotopes enriches seawater in lighter Ca isotopes. In contrast, diminishing dolomitization in the ocean enriches seawater in heavier Ca isotopes possibly explaining the gradual increase in the Ca isotope composition of seawater from the Miocene Climatic Optimum (time interval of high atmospheric and seawater temperatures also characterized by large continental shelfs and sub- to anoxic conditions in ocean water between 17 and 15 Ma) to the present.

A sudden increase of the Ca isotope values, such as the one at the beginning of the Late Paleozoic (350 Ma; Fig. 2), correlate with a shift from the Early Paleozoic calcitic sea to the Late Paleozoic aragonitic sea. Ca isotope fractionation is offset by about 0.5 ‰ between calcite and aragonite, so the shift from a calcite- to an aragonite-dominated ocean would be expected to cause a shift in the seawater Ca isotope composition.

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